Visible-light Photocatalysis in Nitrogen-doped Titanium Oxides

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While TiO_2, on which most of the photocatalytic studies have been focused, shows relatively high reactivity and chemical stability under ultraviolet (UV) light (larger than the band gap of 3.2 eV in the anatase crystalline phase or the wavelength λ<387 nm), new development of photocatalysts that can yield high reactivity under visible light (λ>380 nm) has been desired to make use of the main part of the solar power, and to extend their applications to living space under relatively poor illumination of interior lighting. Here we present properties in N doped TiO_2, showing a significant improvement over TiO_2 in photocatalytic activity under visible light.

$TiO_{2-x}N_x$ films, which were prepared by sputtering the TiO_2 target in N_2 (40%)/Ar gas mixture, have noticeably absorbed visible light (λ<500 nm) where the TiO_2 films have not. Photocatalytic activity has been evaluated by measuring decomposition rates of methylene blue as a function of the cutoff wavelength of the optical high-path filters under fluorescent light (Fig. 1). We have also evaluated photodecompositions of gaseous acetaldehyde and contact angles of water on the sample films under interior lighting. These results clearly show that the photocatalytic activity of the $TiO_{2-x}N_x$ samples are superior to that of the TiO_2 samples in the visible range of irradiation, while the both samples yield similar activity in the UV range of irradiation.

We have also calculated densities of states for the doping of (C, N, F, P, or S) in the anatase TiO_2 crystal, by the full-potential linearized augmented plane wave formalism in the framework of the local density approximation. Among these materials, the substitutional doping of N for O has proven effective for the band-gap narrowing and the visible-light photocatalytic activity as N 2*p* states mix with O 2*p* states in the valence bands. On the other hand, molecularly chemisorbed states along with the interstitial doping of N hardly amalgamate with the band states of TiO_2, and are thus unlikely effective for photocatalysis. These insights are indeed consistent with experimental results including X-ray photoemission spectroscopy studies.

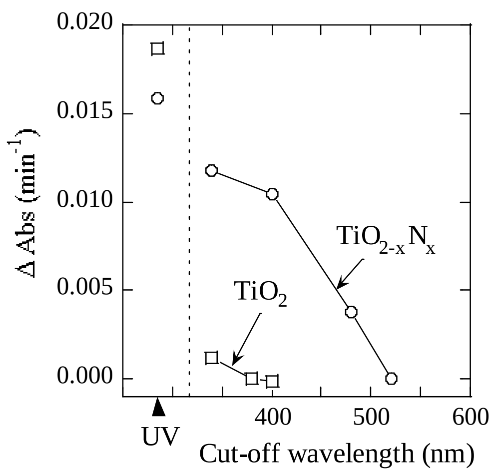

Fig. 1 Photodecompositions of methylene blue